

Conductive polymer

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A **conductive polymer** is an [organic polymer semiconductor](#), or an [organic semiconductor](#). Roughly, there are two classes— the [Charge transfer complexes](#) and the [conductive polyacetylenes](#). The latter include [polyacetylene](#) itself as well as [polypyrrole](#), [polyaniline](#), and their derivatives.

Most commercially produced [organic polymers](#) are [electrical insulators](#). [Conductive organic polymers](#) often have extended [delocalized bonds](#) (often composed of [aromatic units](#)). At least locally, these create a band structure similar to [silicon](#), but with [localized states](#). When [charge carriers](#) (from the addition or removal of [electrons](#)) are introduced into the conduction or valence bands (see below) the [electrical conductivity](#) increases dramatically. Technically almost all known [conductive polymers](#) are [semiconductors](#) due to the band structure and low [electronic mobility](#). However, so-called [zero band gap](#) [conductive polymers](#) may behave like [metals](#). The most notable difference between [conductive polymers](#) and [inorganic semiconductors](#) is the [mobility](#), which until very recently was dramatically lower in [conductive polymers](#) than their [inorganic counterparts](#), though recent advancements in [molecular self-assembly](#) are closing that gap.

[Delocalization](#) can be accomplished by forming a [conjugated backbone](#) of continuous overlapping orbitals. For example, alternating single and double carbon-carbon [bonds](#) can form a continuous path of overlapping [p orbitals](#). In [polyacetylene](#), but not in most other [conductive polymers](#), this creates [degeneracy](#) in the frontier molecular orbitals (the highest occupied and lowest unoccupied orbitals named [HOMO](#) and [LUMO](#) respectively). This leads to the filled ([electron containing](#)) and unfilled bands ([valence](#) and [conduction bands](#) respectively) resulting in a [semiconductor](#).

However, [conductive polymers](#) generally exhibit very low conductivities. In fact, as with [inorganic amorphous semiconductors](#), conduction in such relatively disordered materials is mostly a function of "[mobility gaps](#)" with [phonon](#)-assisted hopping, [polaron](#)-assisted [tunnelling](#), etc. between [localized states](#) and not band gaps as in [crystalline semiconductors](#).

In more ordered materials, it is not until an electron is removed from the valence band ([p-doping](#)) or added to the conduction band ([n-doping](#), which is far less common) does a [conducting polymer](#) become highly conductive. [Doping](#) (p or n) generates [charge carriers](#) which move in an [electric field](#). Positive charges ([holes](#)) and negative charges ([electrons](#)) move to opposite electrodes. This movement of charge is what is actually responsible for [electrical conductivity](#) in [crystalline materials](#).

In contrast, typically "doping" in the polyacetylene-derived conductive polymers involves actually oxidizing the compound. Conductive organic polymers associated with a protic solvent may also be "self-doped". Melanin is the classic example of both types of doping, being both an oxidized polyacetylene and likewise commonly being hydrated.

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[edit] History



voltage-controlled switch, an organic polymer electronic device from 1974. Now in the Smithsonian.

See *An Overview of the First Half-Century of Molecular Electronics* by Noel S. Hush, *Ann. N.Y. Acad. Sci.* 1006: 1–20 (2003)

In 1963, Australians DE Weiss and coworkers reported ^[1] high conductivity in oxidized iodine-doped polypyrrole, a polyacetylene derivative. They achieved the quite low resistivity of 1.0 ohm-cm. In a series of detailed papers, they also described the effects of

doping with iodine on conductivity, the conductivity type (n or p), and electron spin resonance studies on polypyrrole. The same authors noted an Australia patent application (5246/61, June 5, 1961) for conducting polypyrrole. In 1965 ^[2] ^[3], the Australian group reached resistances as low as .03 ohm/cm with other conductive polymers. This is roughly equivalent to present-day efforts. This extensive work was "lost" until recently. E.g., Diaz *et al.* ^[4] are often wrongly credited with discovering conductive polypyrrole in 1979.

In an "active" solid-state device, a current or voltage controls current flow. In 1974, as a "proof of concept" for their version of the now-accepted model of conduction in such materials, John McGinness and his coworkers built and reported ^[5] a voltage-controlled organic-polymer switch. This device used melanin— here, a self-doped mixed copolymer of oxidized polyacetylene, polypyrrole and polyaniline. It is now in the Smithsonian's collection of early electronic devices. In the "ON" state, this material has almost metallic conductivity. As Hush notes, this device also exhibited negative differential resistance, now a well-characterized hallmark of electronically-active organic materials. Though in a major journal and (e.g.) the subject of a contemporary news article ^[6] in the journal *Nature*, this work was also "lost" until similar devices emerged decades later.

It is unclear if the Nobel committee in awarding the 2000 Nobel prize in chemistry considered these earlier works. See Nobel Prize controversies.

[edit] Nobel Prize

In a reprise of Weiss' *et al.*'s earlier work with polypyrrole, in 1977 Hideki Shirakawa, Alan G. MacDiarmid, Alan J. Heeger and coworkers reported ^[7] high conductivity in similarly oxidized, iodine-"doped" polyacetylene. This work eventually resulted in the award to them of the 2000 Nobel prize in Chemistry. According to the citation, this was "*For the discovery and development of conductive polymers*" ^[8].

[edit] Chemistry

Common classes of organic conductive polymers include poly(acetylene)s, poly(pyrrole)s, poly(thiophene)s, poly(aniline)s, poly(fluorene)s, poly(3-alkylthiophene)s, polytetrathiafulvalenes, polynaphthalenes, poly(p-phenylene sulfide), and poly(para-phenylene vinylene)s. Classically, these linear backbone polymers are known as polyacetylene, polyaniline, etc. "blacks" or "melanins". The melanin pigment in animals is generally a mixed copolymer of polyacetylene, polypyrrole, and polyaniline. Some fungal melanins are pure polyacetylene.

[edit] Doping

In silicon semiconductors, a few of the silicon atoms are replaced by electron rich (e.g., phosphorus) or electron-poor (e.g. boron) atoms to create n-type and p-type semiconductors, respectively. In contrast, there are two primary methods of doping a conductive polymer, both through an oxidation-reduction (redox) process. The first method, chemical doping, involves exposing a polymer, such as melanin (typically a thin film), to an oxidant (typically iodine or bromine) or reductant (far less common, but typically involves alkali metals). The second is electrochemical doping in which a polymer-coated, working electrode is suspended in an electrolyte solution in which the polymer is insoluble along with separate counter and reference electrodes. An electric potential difference is created between the electrodes which causes a charge (and the appropriate counter ion from the electrolyte) to enter the polymer in the form of electron addition (n doping) or removal (p doping). Polymers may also be self-doped, e.g., when associated with a protonic solvent such as water or an alcohol.

The reason n doping is so much less common is that Earth's atmosphere is oxygen-rich, which creates an oxidizing environment. An electron-rich n doped polymer will react immediately with elemental oxygen to de-dope (re-oxidize to the neutral state) the polymer. Thus, chemical n doping has to be done in an environment of inert gas (e.g., argon). Electrochemical n doping is far less common in research, because it is much more difficult to exclude oxygen from a solvent in a sealed flask; therefore, although very useful, there are likely to be no commercialized n doped conductive polymers.

[edit] Electroluminescence

Electroluminescence and photoconductivity in organic compounds has been known since the early 1950's. However, the very poor conductivity of such materials limited current flow and thus light output. In contrast, the increased current flow through conductive polymers and improvements in their efficiency has led to the rapid development of practical polymer-based light emitting devices (OLEDs) and organic photovoltaic devices.

[edit] Properties

The biggest advantage of conductive polymers is their processibility. Conductive polymers are also plastics (which are organic polymers) and therefore can combine the mechanical properties (flexibility, toughness, malleability, elasticity, etc.) of plastics with the high electrical conductivities of a doped conjugated polymer.

[edit] Physics

In addition to "switching", an increase in conductivity can also be accomplished in a field effect transistor (organic FET or OFET), or by irradiation (originally-demonstrated in the 1960's ^[2]). Strong coupling can also occur between electrons and phonons (mechanical

oscillations such as heat vibrations, particles of sound) since both are constrained to travel along the polymer backbone.

[edit] Applications of conducting polymers

Electroluminescence (light emission) in organic compounds has been known since the early 1950's, when Bernanose and coworkers first produced electroluminescence in crystalline thin films of acridine orange and quinacrine. In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doping. In some cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. The increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This has led to the development of flat panel displays using OLEDs, solar panels and optical amplifiers. Conducting polymers are also successfully used as active matrix of polymer solar cells.

[edit] Biological applications

Conductive polymers such as DOPA melanin are present in most mammalian tissues where electrical conduction or transduction from light or sound are necessary, including the skin, eye, inner ear, and Midbrain. Melanin's electronic conductivity and allied phenomena such as strong electron-phonon coupling seems to be the underlying mechanism for absorption of light, and electron-phonon interactions are exploited in hearing ^[10]. See the main article: Melanin.

[edit] Current Research

The European Union is currently funding a pan-European project into the development of conductive Polymers. The Polycondproject involves a consortium of trade associations and SME's from across Europe and is due for completion in January 2009. The main aim for this project is to develop conductive polymer products that have embedded and improved Electromagnetic Interference (EMI) and Electrostatic Discharge (ESD) protection. Research is now at an advanced stage and prototypes of products have been produced and are now being taken through a rigorous testing process to assess the Polymers performance and characterize it. PERC(Polymer Electronics Research Center) at University of Auckland is developing a range of novel DNA sensor technologies based on conducting polymers, photoluminescent polymers and inorganic nanocrystals (Quantum Dots) for simple, rapid and sensitive gene detection.

[edit] See also

- Organic semiconductor
- Molecular electronics
- "An Overview of the First Half-Century of Molecular Electronics" by Noel S. Hush, *Ann. N.Y. Acad. Sci.* 1006: 1–20 (2003).
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- Australian Journal of Chemistry, 1963 16: 1056-89
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4. ^ http://www.rsc.org/delivery/_ArticleLinking/DisplayArticleForFree.cfm?doi=C39790000635&JournalCode=C3
5. ^ Semiconductor Switching in Melanins
6. ^ High Conductivity Organic Semiconductor
7. ^ Journal of the Chemical Society, Chemical Communications articles
8. ^ Chemistry 2000
9. ^ <http://www.drproctor.com/os/photoconductivity.htm>
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